The Spectrum of Beryllium Fluoride.

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[PLATE 3.]

1. *Introductory.*

In a previous communication,[*] an account was given of an investigation of the spectra of the fluorides of magnesium, calcium, strontium, and barium, which was undertaken with a view to determine the numerical relations existing between these spectra. It was shown that the homologous series of the different spectra can be connected by empirical equations, involving only the constants of the series equations and the molecular weights or the molecular numbers of the respective compounds. It therefore seemed desirable to extend the investigation in order to ascertain if these relations are maintained in the spectrum of beryllium fluoride. Unlike the other alkaline earth compounds, the spectra of compounds of beryllium have previously received but little attention, and it has even remained doubtful[†] whether the well-known groups of bands between λ 4426 and λ 5446 belong to the element itself or to the oxide. The present investigation has special reference to the spectrum of beryllium fluoride, which has not previously been recorded.

2. *Experimental.*

Photographs of the spectrum were taken with a 10-feet concave grating, and also with a quartz spectrograph of considerable dispersion (about 5·6 A. per millimetre at λ 2900). The source of light was an ordinary carbon arc fed with beryllium potassium fluoride, this being the only salt in which BeF_2 was available. The presence of potassium does not interfere with the band spectrum of BeF_2, as was proved by a photograph of the spectrum of the arc when fed with potassium fluoride only. In order to distinguish the bands of the fluoride from those of the oxide, direct comparison spectrograms of BeF_2 and BeO_2 were prepared. Fortunately, BeO_2 does not present any spectrum in the vicinity of the fluoride bands. The bands in question can therefore be safely attributed to the fluoride.

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[*] 'Roy. Soc. Proc.,' A, vol. 99, p. 436.

[†] H. Kayser, 'Handbuch der Spectroscopie,' vol. 5, p. 162.

As before, the arc was extended to a flame by admixture of sodium carbonate, and only the outer edge of its image was thrown upon the slit. Measurements of the spectrograms were made in the usual way with an iron comparison, using the wave-lengths of the iron lines as given in Burns' Table. The wave-lengths of the band heads have been determined independently from the spectrograms obtained with the concave grating in the second order and the quartz spectrograph. The means of the two concordant sets have been adopted.

3. *Results.*

In the region investigated, namely, between λ 2200 and λ 6700, BeF_2 presents six groups of bands. These are all in the ultra-violet, as is to be expected on account of the small molecular weight, and all fade off towards the red (see Plate 3). Proceeding towards the long wave-length side, each of the first four groups consists of alternating bright and faint heads, and the bright one is resolved into two heads under high dispersion. In the fifth group the corresponding faint series is missing. In the sixth group seven heads have been accurately measured, but they could not be arranged in series similar to the others. The second, third, and fourth groups are the most intense. The nomenclature adopted is that previously used for the groups of MgF_2 of similar structure. The six groups are thus denominated as E_1, E_2, E_3, E_4, E_5, and E_6. Details of the measurements are given in Table I, which also shows the differences (O — C) between the observed wave-numbers and those calculated from equations of the type

$$\nu = a - bm - cm^2.$$

4. *Structure of the Band* λ 3009·85.

As all the bands appeared to be of similar structure, the most intense one at λ 3009·85 was selected for a more detailed investigation. This was photographed in the third order of the grating, giving resolution and definition permitting a satisfactory study of the structure of the band. It was then observed that of the close pair of heads, the outer one on the more refrangible side consists of a single line followed by an apparently continuous spectrum stretching across the interval between the pair. The second head is associated with a series of fine lines, all of which, with the exception of the one next to the head itself, were clearly separated, and could therefore be accurately measured. Starting from the head, the distance from line to line gradually increases, the rate of increase being fairly uniform up to $m = 7$, and subsequently decreasing for the next two members. The lines are fairly sharp to start with, as such lines usually are, but with increasing values of m they

Table I.—Bands of Beryllium Fluoride.

Series.	m.	λ I.A. (air).	$\nu_{\text{obs.}}$ (vac.).	$\nu_{\text{obs.}} - \nu_{\text{cal.}}$
E_1	0	2815·95	35501·66	0·00
	1	26·20	372·81	−0·03
	2	36·31	246·76	+1·18
	3	46·55	120·01	+0·13
	4	56·65	34995·87	+0·13
	5	66·66	873·58	+0·42
	6	76·68	752·15	+0·21
	7	86·59	632·75	+0·07
	8	96·90	510·72	−4·06
E_1'	0	2816·33	35496·87	0·00
	1	26·53	368·67	+0·02
	2	36·69	242·05	+0·06
	3	46·78	117·04	+0·15
	4	56·86	34993·29	−0·06
	5	66·87	871·03	−0·34
	6	76·86	749·97	−0·98
E_1''	0	2818·26	35472·44	0·00
	1	28·41	345·18	+0·04
	2	38·61	218·21	−0·23
	3	48·78	092·39	−0·05
	4	59·02	34966·74	−0·10
	5	69·36	840·78	−1·16
	6	79·48	718·37	+0·73
E_2	0	2908·94	34366·73	0·00
	1	18·39	255·49	0·00
	2	27·77	145·78	+0·01
	3	37·07	037·69	+0·12
	4	46·33	33930·89	−0·27
	5	55·69	825·49	−0·24
E_2'	0	2909·32	34362·25	0·00
	1	18·74	251·27	+0·06
	2	28·09	142·07	−0·12
	3	37·28	035·14	+0·25
E_2''	0	2911·80	34333·00	0·00
	1	20·99	225·01	0·00
	2	30·13	118·17	+0·13
	3	39·18	013·15	+0·06
E_3	0	3009·58	33217·51	0·00
	1	17·97	125·20	0·00
	2	26·40	032·96	−0·04
	3	34·88	32940·68	0·00
E_3'	0	3009·85	33214·65	0·00
	1	18·34	121·25	0·00
	2	26·86	027·93	−0·04
	3	35·41	32934·82	+0·01
E_3''	0	3012·99	33180·04	
	1	20·34	099·32	
	2	—	rather hazy	
	3	—	,,	

Table I—(*continued*).

Series.	m.	λ I.A. (air).	$\nu_{obs.}$ (vac.).	$\nu_{obs.} - \nu_{cal.}$
E_4	0	3126·06	31979·95	0·00
	1	33·44	904·64	0·00
	2	40·78	830·10	+0·09
	3	48·09	756·11	+0·05
	4	55·37	682·79	+0·07
	5	62·38	610·56	+0·36
	6	69·84	538·28	−0·01
	7	76·99	467·32	+0·26
	8	84·15	396·58	+0·15
	9	91·28	326·36	−0·39
	10	98·34	257·22	−0·23
E_4'	0	3126·35	31976·88	0·00
	1	33·72	901·80	0·00
	2	41·05	827·26	+0·02
	3	48·42	752·79	−0·41
	4	55·71	679·46	−0·22
	5	62·98	606·66	−0·02
	6	70·22	534·50	+0·30
	7	77·46	462·57	+0·33
E_4''	0	3130·79	31931·64	0·00
	1	38·00	858·29	−0·05
	2	45·19	785·39	−0·05
	3	52·40	712·71	−0·23
	4	59·70	639·46	−0·38
	5	66·69	569·64	+0·50
	6	73·89	498·05	+0·21
	7	81·06	426·97	+0·03
E_5	0	3249·24	30767·61	0·00
	1	55·26	710·64	+0·08
	2	61·28	653·97	0·00
	3	67·30	597·50	−0·05
	4	73·26	541·89	−0·75
	5	79·27	485·86	−0·83
	6	85·27	430·14	−1·02
	7	91·36	373·90	−0·48
	8	97·42	318·01	−0·09
	9	303·50	262·22	0·00
	10	09·40	208·28	−0·75
	11	15·54	152·36	+0·27
	12	21·65	096·91	+1·04
	13	27·75	041·76	+1·70
	14	33·93	29986·09	+2·09
E_5'	0	3249·40	30766·10	0·00
	1	55·45	708·84	−0·03
	2	61·50	651·90	0·00
	3	67·50	595·63	−0·26
	4	73·47	539·86	−0·63
	5	79·44	484·28	−0·82
	6	85·43	428·71	−0·63
	7	91·36	373·90	−0·81
	8	97·38	318·47	0·00
	9	03·37	263·60	+0·64
	10	08·25	208·78	+1·60
	11	15·38	154·09	+2·82

Table I.—(*continued*).

Group.	λ I.A.	ν (vac.).	Group.	λ I.A.	ν (vac.).
E_6	3344·12	29894·66	E_6	3371·26	29654·05
	49·93	842·82		78·03	594·55
	61·56	739·60		92·59	467·58
	63·67	720·96			

Constants for calculation of the series are collected in Table II.

Table II.

Series.	$a = \nu_o$.	b.	c.
E_1	35501·66	+129·6	−0·78
E_1'	35496·87	+129·0	−0·78
E_1''	35472·44	+127·6	−0·30
E_2	34366·73	+112·0	−0·76
E_2'	34362·25	+112·0	−0·96
E_2''	34333·00	+108·5	−0·51
E_3	33217·51	+92·326	−0·016
E_3'	33214·65	+93·46	−0·06
E_3''	33180·04	+90·72	—
E_4	31979·95	+75·65	−0·34
E_4'	31976·88	+75·34	−0·26
E_4''	31931·64	+73·50	−0·20
E_5	30767·61	+57·023	−0·1015
E_5	30766·10	+57·482	−0·191
E_6		Not arranged in series.	

gradually become diffuse, and, at $m = 8$, where the change in the interval is a minimum, they merge to a diffuse patch, apparently terminating the series rather abruptly. After this, there begins a fresh set of lines with an abrupt increase in the interval, which continues regular as far as the lines could be traced; the identification of the last four members is somewhat uncertain owing to the superposition of lines belonging to the band λ 3012·99, which begins here. This new set of lines also begins with characteristic sharpness, but gradually becomes diffuse and separates into two different series with increasing values of m. The first nine lines thus form a series of short range and the rest form two other series, which coalesce at the beginning.

The structure is shown by the curve in fig. 1, which represents the varying distances between successive lines in the three series plotted against successive integral values of m. As may be seen from the curve, none of the series agree throughout their whole length with the linear form implied by the usual formula, but the introduction of a fourth constant with m^3 gives a much

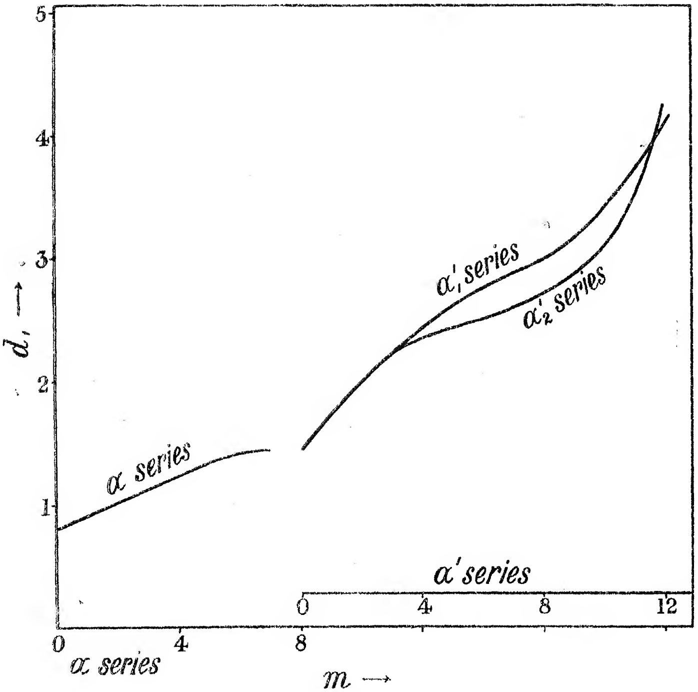


FIG. 1.

closer agreement between the observed and the calculated values. The numerical equations of the various series are :—

$$\text{Series } \alpha \quad \ldots \quad \nu = 33214{\cdot}65 - 0{\cdot}7259m - 0{\cdot}0525m^2 - 0{\cdot}00015m^3$$

$$\text{Series } \alpha_1' \quad \ldots \quad \nu = 33204{\cdot}05 - 1{\cdot}624m - 0{\cdot}125m^2 + 0{\cdot}0022m^3$$

$$\text{Series } \alpha_2' \quad \ldots \quad \nu = 33204{\cdot}05 - 1{\cdot}6235m - 0{\cdot}102m^2 + 0{\cdot}0013m^3.$$

Data for the consideration of regularity in the band are collected in Table III which also shows the differences between the observed and the calculated wave-numbers in the last column. The greatest deviation in wave-number is 0·57, corresponding to a difference of 0·05 A. between the observed and calculated wave-lengths. The error, however, is sufficiently systematic to indicate the imperfection of the formula.

5. *The Relation with the Spectra of other Alkaline Earth Fluorides.*

Each group of BeF_2 bands is composed of alternating double and single heads, and as such the only similarity which they present to the spectra of the other alkaline earth fluorides is with that of the E_1 group of MgF_2. But, while presenting the same appearance, the bands of BeF_2 fade off towards the red, whereas the bands of MgF_2 fade off in the opposite way. For the present,

Table III.—The Series α, α' of the Band λ 3009·85.

α Series.

m.	λ I.A.	ν (vac.).	d_1.	$\nu_{obs.} - \nu_{cal.}$
0	3009·85	33214·65	0·78	0·00*
1	09·92	213·87	0·89	0·00*
2	10·00	212·98	0·99	0·00
3	10·09	211·99	1·10	−0·01
4	10·18	210·89	1·22	0·00
5	10·29	209·67	1·32	−0·02
6	10·41	208·35	1·42	−0·01
7	10·54	206·93	1·45	0·00*
8	10·67	205·48		+0·08

α_1' Series.

m.	λ I.A.	ν (vac.).	d_1.	$\nu_{obs.} - \nu_{cal.}$
0	3010·80	33204·05	1·75	0·00
1	10·96	202·30	1·99	0·00
2	11·14	200·31	2·20	0·00
3	11·34	198·11	2·43	0·00
4	11·56	195·68	2·64	−0·01
5	11·80	193·04	2·76	−0·04
6	12·05	190·28	2·87	0·00
7	12·31	187·41	2·97	+0·10
8	12·58	184·44	3·18	+0·26
9	12·86	181·26	3·42	+0·35
10	13·18	177·84	3·74	+0·33
11	13·52	174·10	4·08	+0·11
12	13·89	170·02		−0·34

α_2' Series.

m.	λ I.A.	ν (vac.).	d_1.	$\nu_{obs.} - \nu_{cal.}$
0	3010·80	33204·05	1·75	0·00
1	10·96	202·30	1·99	−0·02
2	11·14	200·31	2·20	−0·09
3	11·34	198·11	2·43	−0·19
4	11·56	195·68	2·43	−0·33
5	11·78	193·25	2·51	−0·29
6	12·01	190·74	2·55	−0·18
7	12·12	188·19	2·76	+0·06
8	12·49	185·43	2·86	+0·23
9	12·75	182·57	3·08	+0·43
10	13·03	179·49	3·52	+0·57
11	13·35	175·97	4·30	+0·39
12	13·75	171·67		−0·46

* Used for the calculation of constants.

however, it seems permissible to identify homologous groups by their actual structure, without taking into consideration the direction in which they fade off. This seems to be confirmed by the fact, pointed out in the previous paper, that the value of the constant for class C, calculated from the suggested formula, is very close to that for class A, although these two classes of bands fade off in the opposite direction.

Taking therefore the bands of BeF_2 to be similar to those of the E_1 group of MgF_2, the previous formula

$$\frac{\log b \times \log M}{a} = \text{constant}$$

agrees fairly satisfactorily, as will be seen from Table IV. As before, a and b are constants used for the calculation of series, and M is the molecular number.

Table IV.

Homologous series.	$a = \nu_0$.	b.	M.	$\frac{\log b \times \log M}{a}$.
MgF_2 E_1	27149·43	36·475	30	$8·50 \times 10^{-5}$
,, E_1'	27145·44	36·435	30	8·50
,, E_1''	27123·57	36·7101	30	8·52
BeF_2 E_1	35501·66	129·6	22	7·99
,, E_1'	35496·87	129·0	22	7·98
,, E_1''	35472·44	127·6	22	7·97
,, E_2	34366·73	112·0	22	8·01
,, E_2'	34362·25	112·0	22	8·01
,, E_2''	34333·00	108·5	22	8·01
,, E_3	33217·51	92·326	22	7·94
,, E_3'	33214·65	93·46	22	7·96
,, E_3''	33180·04	90·72	22	7·92
,, E_4	31979·95	75·65	22	7·89
,, E_4'	31976·88	75·34	22	7·88
,, E_4''	31931 64	73·50	22	7·85

Considering the approximate character of the formula adopted, and the wide range of the values of a, b, and M, the calculated constants agree as closely as could be expected.

Summary.

1. The spectrum of beryllium fluoride, hitherto unrecorded, has been investigated. It has been found to consist of six groups of bands, all in the ultra-violet between λ 2800 and λ 3400, and all fading off towards the red.

2. The strongest band at λ 3009 has been investigated in detail, and has been found to include three series of lines, which depart considerably from the usual type of formula.

3. The groups of bands have been found to be similar to one of the groups of magnesium fluoride, and are related to this group in accordance with the formula for alkaline earth fluorides proposed in a previous paper.

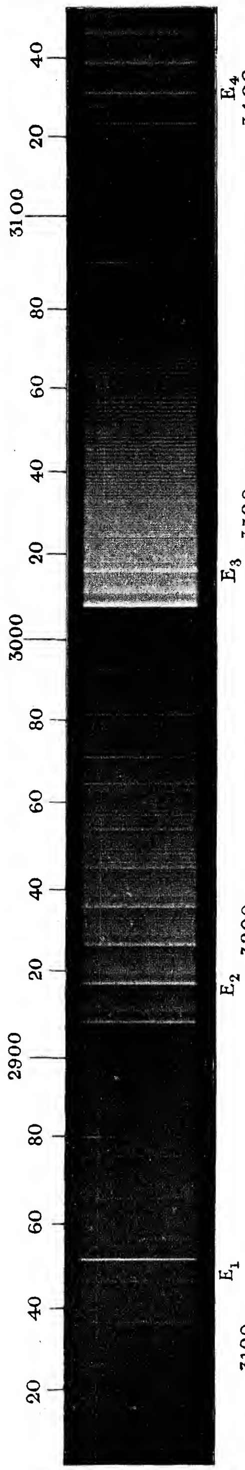
In conclusion, I beg to record my thanks to Prof. A. Fowler, F.R.S., for the kind interest he always takes in my work.

DESCRIPTION OF THE PLATE.

(*a*) Spectrum of beryllium fluoride between λ 2820 and λ 3140, showing the groups E_1, E_2, E_3, and a part of E_4.

(*b*) Spectrum of beryllium fluoride between λ 3100 and λ 3400, showing the groups E_4 and E_5.

(*c*) Spectrum of beryllium fluoride, group E_3, showing the structure of the band λ 3009·85 with the iron comparison at the top.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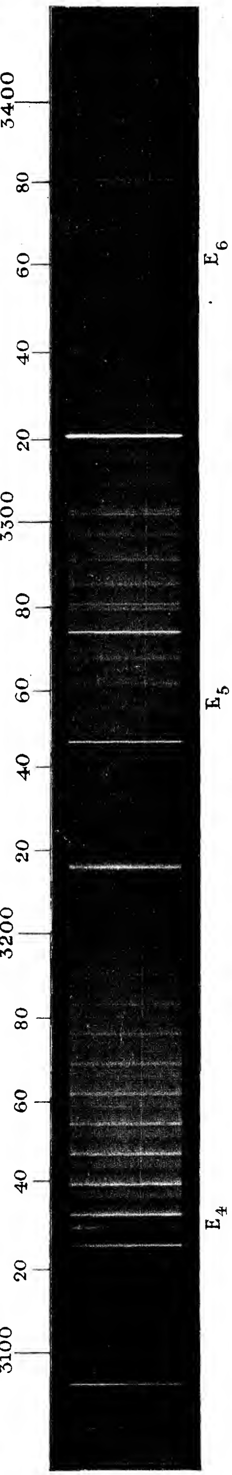
(a)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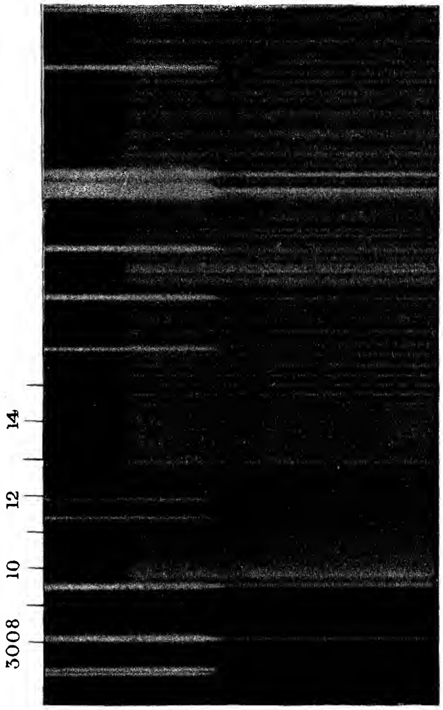
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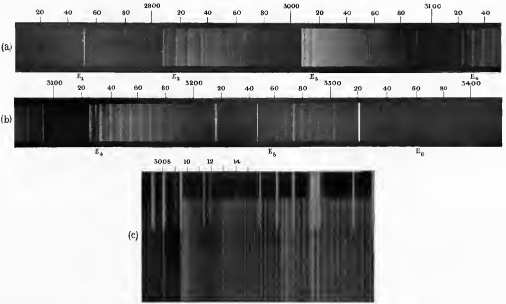
(c)



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